Chemistry of Heterocyclic Compounds, Vol. 42, No. 11, 2006

LETTERS TO THE EDITOR

2,5,2',5'-TETRAHYDRO[3,3']BIFURANYL. A NOVEL HETEROCYCLIC SYSTEM FROM 2-BUTENE-1,4-DIOL

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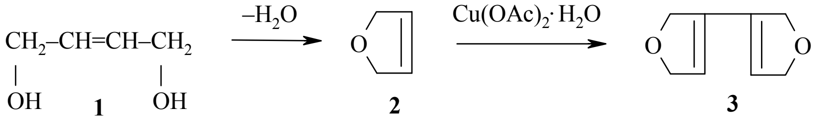
Keywords: copper acetate, 2-butene-1,4-diol, 2,5-dihydrofuran, dimerization, cyclodehydration.

Hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol (**1**) on suspended palladium catalysts at atmospheric pressure is accompanied by the formation of side products (*n*-butanol, γ-hydroxybutyraldehyde, and others [1]) but the main loss of target compound is seen at the stages of distillation of water and the vacuum fractionation of the hydrogenation catalyzate as a result of polymerization of compound **1**. With the aim of stabilizing the 2-butene-1,4-diol copper acetate monohydrate was added to the reaction product. Upon distillation the overhead fractions unexpectedly showed the presence of a novel side product which was separated and identified as 2,5,2'5'-tetrahydro[3,3']bifuranyl (**3**). A possible mechanism for its formation includes a stage of cyclodehydration of diol **1** and a Glaser type oxidative dimerization of the 2,5-dihydrofuran (**2**).



1 **2** **3**

The structure of the novel heterocyclic system **3** was confirmed by physicochemical methods and by a counter synthesis.

IR spectra were taken on a Specord IR-75 instrument using vaseline oil. The ^{1}H NMR spectra were obtained on a Varian Unity-300 (300 MHz) machine using $CDCl_3$ relative to the residual solvent signal at 7.26 ppm. Mass spectra were taken on a Varian MAT-3 instrument using EI (70 eV).

2,5-Dihydrofuran (2). The catalyst (2% Pd/C, 0.1 g) was added with stirring to 2-butene-1,4-diol (**1**, 39.8 g, 0.45 mol). The mixture was heated above 100°C and the 2,5-dihydrofuran raw material was distilled off until less that about 5 ml of liquid remained in the flask. The raw material was then distilled and the fraction with bp 53-56°C was collected to give the 2,5-dihydrofuran (21.4 g, 66%). The product was identical to that prepared by the catalytic dehydration of 2-butene-1,4-diol **1** in [3].

2,5,2',5'-Tetrahydro[3,3']bifuranyl (3). A. The overhead fraction in the distillation of compound **1** (50 ml) was held in a cold compartment for about 6 days. The precipitate formed was separated, washed with

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cold water, and dried in a vacuum desiccator to give compound **3** with mp 94-96°C (from water). IR spectrum, ν, cm^{-1}: 1605 (C=C), 997, 985, 946 (C–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.76 (8H, m, CH_2); 5.79 (2H, m, HC=C). Mass spectrum, *m/z* (I_{rel}, %): 138 $[M]^+$ (100), 109 $[M\text{-}COH]^+$ (12), 108 $[M\text{-}CO]^+$ (9). Found, %: C 69.42; H 23.27. $C_8H_{10}O_2$. Calculated, %: C 69.55; H 23.16.

B. Compound **3** was also prepared by a counter synthesis. A mixture of compound **2** (7.0 g, 0.1 mol), copper acetate monohydrate (27.5 g, 0.14 mol), pyridine (50 ml), and methanol (50 ml) was refluxed for 2 h. The dark blue suspension turned green. The cooled reaction mixture was then acidified with sulfuric acid (d = 1.83) with stirring , cooled, and extracted with dichloromethane. The residue obtained after evaporation of the solvent was recrystallized from water to give compound **3** (3.86 g, 56%) with mp 95-96^{o}C. Found, %: C 69.62; H 23.25. $C_8H_{10}O_2$. Calculated, %: C 69.55; H 23.16. A mixture of the mixture of substances obtained by methods A and B did not give a depression of melting point and the IR and ^{1}H NMR spectra were identical.

The work was carried out with the financial support of the Russian Fund for Basic Research (grant 04 03-32485).

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